

ULTRA SUPERCRITICAL STEAMSIDE OXIDATION

G. R. Holcomb

S. D. Cramer

B. S. Covino, Jr.

S. J. Bullard

M. Ziomek-Moroz

Albany Research Center, U. S. Department of Energy

1450 Queen Avenue SW

Albany, OR 97321

ULTRA SUPERCRITICAL STEAMSIDE OXIDATION

G. R. Holcomb

S. D. Cramer

B. S. Covino, Jr.

S. J. Bullard

M. Ziomek-Moroz

Albany Research Center, U. S. Department of Energy

1450 Queen Avenue SW

Albany, OR 97321

Abstract

Ultra supercritical (USC) power plants offer the promise of higher efficiencies and lower emissions, which are goals of the U.S. Department of Energy's Advanced Power Systems Initiatives. Most current coal power plants in the U.S. operate at a maximum steam temperature of 538°C. However, new supercritical plants worldwide are being brought into service with steam temperatures of up to 620°C. Current Advanced Power Systems goals include coal generation at 60% efficiency, which require steam temperatures of up to 760°C. This research examines the steamside oxidation of advanced alloys for use in USC systems, with emphasis placed on alloys for high- and intermediate-pressure turbine sections. Initial results of this research are presented.

Introduction

For many years the temperatures and pressures of steam boilers and turbines were intentionally increased. These increases allowed for greater efficiencies in steam and power production, and were enabled by improvements in materials properties such as high temperature strength, creep resistance, and oxidation resistance. From 1910 to 1960, there was an average increase in steam temperature of 10°C per year, with a corresponding increase in plant thermal efficiency from less than 10% to 40% (1). The first commercial boiler with a steam pressure above the critical value of 22.1 MPa (3208 psi) was the 125 MW Babcock & Wilcox (B&W) Universal Pressure steam generator in 1957—located at the Ohio Power Company's Philo 6 plant (2). Since 1960 in the United States, the overall trend of increasing temperatures and pressures has stopped and stabilized at about 538°C and 24.1 MPa (3). In Europe and Japan, where fuel costs are a higher fraction of the cost of electricity, temperatures and pressures continued to rise. An example of a state of the art power plant in Europe is the Westfalen (2004) plant, with steam conditions of 31.0 MPa/593°C/621°C (4). It has a net plant efficiency of 43.5%, compared to 37% for a typical subcritical 16.5 MPa/538°C/ 538°C plant (4). Today there is again interest in the United

States for advanced supercritical power plants. Large increases in the cost of natural gas have led to the reexamination of coal power plants, and advanced supercritical plants offer advantages in lower fuel costs and lower emissions of SO_x , NO_x , and CO_2 (5). Current U.S. Department of Energy research programs are aimed at 60% efficiency from coal generation, which would require increasing the operating conditions to as high as 760°C and 37.9 MPa. In general terms, plants operating above 24 MPa/593°C are regarded as ultra supercritical (USC), those operating below 24 MPa as subcritical, and those at or above 24 MPa as supercritical (SC) (3).

In the past thirty years, advances in the high temperature strength of ferritic steels have allowed for the increase of operating temperatures and pressures, but without the thermal fatigue issues of the austenitic steels that had to be used to obtain the required high temperature strengths in the early 1960s. Ferritic steels, as used here, refers to the equilibrium structure. In practice, a martensitic or partially martensitic structure is obtained from heat-treating. The upper temperature for use of ferritic steels appears to be limited to about 620 to 630°C. For temperatures above 630°C, the most promising candidate alloys are nickel-base superalloys.

The purpose of this paper is to report on research that examines the steamside oxidation of advanced alloys for use in supercritical turbine systems. Low-pressure turbine sections of USC systems would not be expected to differ from current designs, so emphasis is placed on alloys for high- and intermediate-pressure turbine sections. Initial results are presented.

Benefits

The driving force for increased operating temperatures and pressures has been increased efficiency in power generation. Recently, an additional recognized benefit has been decreased CO_2 emissions. Estimates of the cost effectiveness of various ways to improve the efficiency of power plants are shown in Table 1. Table 1 shows that increasing the steam temperature is one of the more cost effective ways of increasing efficiency, while increasing the steam pressure is less effective.

For reduced CO_2 emissions, calculations by Booras *et al.* (6) indicate that a subcritical 37% efficient plant 500 MW plant burning Pittsburgh #8 coal would produce about 850 tons of CO_2 per kWh. Ultra supercritical plants at 43% and 48% efficiency would respectively produce about 750 and 650 tons of CO_2 per kWh.

Research Approach

The research presented here aims to bridge the gap in information between the various steam conditions to study the steamside oxidation resistance of target alloys. To be examined are the effects from steam temperature, steam pressure, and, to a limited extent, the effect of sample curvature. The curvature can modify the spallation behavior of oxides by changing the stress fields that are the driving force to detach part or all of the scale. The importance of steam chemistry is also recognized, and will be controlled during supercritical steam exposures.

Table 1: Cost effectiveness of methods to improve fossil fuel power plant efficiency (3).
Cost is in terms of millions of U.S. Dollars per net percent increase in lower heating value (LHV) efficiency.

Rank	Method	Cost
1	Reducing condenser back pressure	3.1
2	Increase to 8th extraction point feed water heater, raising feed water temperature	3.8
3	Raising live steam and reheat temperatures	8.3
4	Raising live steam temperature	8.6
5	Using separate boiler feed pump turbine (BFPT) instead of main turbine driven pump	9.6
6	Raising live steam pressure	25.1
7	Change from single to double reheat	38.2
8	Using separate BFPT condenser	41

The results presented here include research in progress from cyclic oxidation in moist air, thermogravimetric analysis in steam, and furnace exposures in moist air. Details of the experimental plans for supercritical exposures have been described elsewhere (7).

Alloys

Various alloys are of interest for use in USC turbine applications. The nominal compositions of these alloys are given in Table 2. A subset of the alloys examined by the Advanced Power System Initiative on USC boilers, selected for examination for USC turbines, include the ferritic alloy SAVE12, the austenitic alloy SUPER 304H, the high Cr and high Ni alloy HR6W, and three nickel-base superalloys Alloy 617, Alloy 230, and Alloy 740. All represent the highest high-temperature strength alloys in their respective alloy classes. Also of interest are four superalloys identified (8-9) as candidates for blade materials for USC conditions: Alloy M-252, Refractory 26, Nimonic 90, and Alloy 718. The superalloy René 41 is included because it is to be the autoclave material for supercritical exposures (7). The last two alloys listed in Table 2, Alloys J1 and J5, were produced for alloy development into solid oxide fuel cells (10). However, Alloy J1 is an equivalent composition to Mitsubishi alloy LTES700, a low coefficient of thermal expansion nickel-base alloy developed for use as fasteners and blades in both current and USC steam turbines (11). Alloy J5 is a modified version of J1.

Table 2: Nominal compositions of alloys of interest for USC turbine applications. References are in parenthesis following the alloy name.

Alloy	Fe	Cr	Ni	Co	Mo	Nb	C	Si	Mn	Ti	Al	Other
SAVE12 (12)	Bal	11		3		0.07	0.10	0.3	0.2			3 W 0.2 V 0.04 Nd 0.04 N
Super 304H (12)	Bal	18	9			0.40	0.10	0.2	0.8			3 Cu 0.1 N
HR6W (12)		23	43			0.18	0.08	0.4	1.2	0.08		6 W 0.003 B
Alloy 617 (13)		22.0	55.0	12.5	9.0		0.07				1.0	
Alloy 230 (13)	<3.0	22.0	55.0	<5.0	2.0		0.10				0.35	14.0 W <0.015 B 0.02 La
Alloy 740 (14)		24	Bal	20		2				2	1	
M-252 (13)	0.75 max	19.0	56.5	10.0	10.0		0.15			2.6	1.0	0.005 B
Refractory 26 (13)	16.0	18.0	38.0	20.0	3.2		0.03			2.6	0.2	0.015 B
Nimonic 90 (13)	1.5	19.5	55.5	18.0			0.06			2.4	1.4	
Alloy 718 (13)	18.5	19.0	52.5		3.0	5.1	0.08 max			0.9	0.5	0.15 Cu max
René 41 (13)	0.3 max	19.0	55.0	11.0	10.0		0.09			3.1	1.5	0.01 B
J1 (10)		12.1	Bal		18					1	0.8	
J5 (10)		12.5	Bal		22				0.5	1		0.04 Y

The alloys considered for these initial tests included SAVE12, HR6W, Alloy 617, Alloy 230, Alloy 740, Rene 41, J1, and J5. There are two versions of the SAVE12 alloy (nominally 11Cr) that were examined: a version corrosion resistant to higher temperatures (10.5Cr), and a higher strength version (9.5Cr). The surface finish on all samples (except where noted) was a polish to

600 grit. A limited number of tests were done on SAVE12 samples that were surface treated on one side with a proprietary treatment to increase oxidation resistance. Curvature effects were examined on SAVE12 (10.5Cr) by machining samples from thick walled pipe. Each of the curvature samples have one curved surface, representing either the inside (concave) or outside (convex) surface of the pipe, Fig. 1. The curved surfaces were machined from as-received pipe (to remove mill-scale) and not subsequently polished to 600 grit.

Cyclic Oxidation

Cyclic oxidation experiments were conducted in air in the presence of steam at atmospheric pressure. This was designed to examine the adhesion and spallation behavior of the protective oxides that form. The tests consisted of 1-hour cycles of heating and cooling (55 minutes in the furnace and 5 minutes out of the furnace) in a tube furnace equipped with a programmable slide to raise and lower the samples, Fig. 2. Water was metered into the bottom of the furnace along with compressed air (50% water vapor-50% air, by volume). The exposure temperature for these initial tests was 760°C. Both flat and curvature samples were examined.



Figure 1. Section of SAVE12 10.5Cr pipe (2-in O.D.) and curvature samples cut from pipe. All but one side of the curvature samples are flat. Samples: concave (left) and convex (right).

Thermogravimetric Analysis (TGA)

Experiments were conducted using thermogravimetric analysis (TGA) with steam at atmospheric pressure. This was designed to obtain information on oxidation kinetics using relatively short (300 hr) test durations. The TGA tests consist of suspending a sample from a Cahn D-101 microbalance in flowing steam for 300 hours at a constant elevated temperature (650-800°C), Fig. 3. Steam is generated by injecting a metered amount of O₂-saturated water into heated tubing to supply a minimum flow rate of 2 mm/s of steam in the reaction chamber. Initial experiments used pure steam. More recent tests used a carrier gas of 60% Ar along with the steam. Even though the presence of Ar is further removed from the actual steam conditions of a power plant, it has been reported (15) that the resulting scale morphologies more closely match industrial conditions than with pure steam alone (for tests conducted at atmospheric pressure).



Figure 2. Cyclic oxidation apparatus for testing in atmospheric pressure steam/air mixtures at up to 800°C.

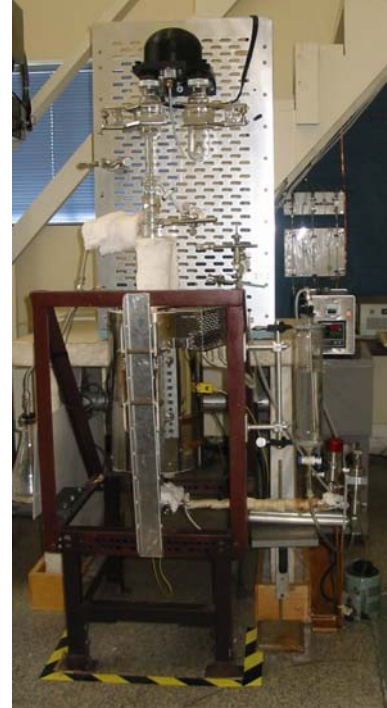


Figure 3. TGA apparatus for testing in atmospheric pressure steam at up to 800°C.

Furnace Exposures

Experiments that expose samples to moist air at atmospheric pressure at 700°C and 800°C were conducted. These tests consist of exposing the samples to air that was bubbled through water, resulting in up to 3% water vapor in the atmosphere. Samples were periodically removed from the furnace for mass measurements, and then replaced in the furnace for further exposure.

Data Analysis

The results thus far consist mainly of changes in sample mass with time. Additional information will later be obtained from microscopic examination of metal-scale cross-sections and from descaling to determine metal loss and maximum penetration rates.

Results and Discussion

Results for cyclic oxidation testing at 760°C are shown in Fig. 4 for the three nickel-base superalloys Alloy 617, Alloy 230, and Alloy 740. The nickel-base superalloys all had an initial mass increase followed by a slow decrease in mass. This indicates a relatively steady rate of

oxide scale loss. The mass change after 100 hours was -0.37 , -1.75 , and $-0.88 \text{ mg/cm}^2\text{y}$, respectively.

There are three pairs of cyclic oxidation results for SAVE12 in Fig. 5. The 10.5Cr-9.5Cr pair was exposed to the largest number of cycles, and after a high initial rate of mass increase have linear oxidation rates of 326 and 296 $\text{mg/cm}^2\text{y}$, respectively. The SAVE12 alloys were exposed at higher temperatures than they were designed for and show large increases in mass with time. The 10.5Cr ST-9.5Cr ST pair had a proprietary surface treatment on one side of each sample. The other side was untreated. They had linear oxidation rates after 100 hours of 281 and 244 $\text{mg/cm}^2\text{y}$, respectively. The last pair consisted of convex and concave samples of SAVE12 with 10.5 Cr. These were cut from tube such that one side was either convex or concave, and the other sides were flat. Neither specimen showed the large initial mass gain of the other two pairs. They have linear oxidation rates after 100 hours of 447 and 22 $\text{mg/cm}^2\text{yr}$, respectively. Based on the low mass change of the concave specimen, the tubes are currently being analyzed for radial homogeneity.

Table 3 summarizes the results of the 300 hr TGA tests in O_2 -saturated steam plus 60%Ar at 800°C . The reaction order and parabolic R^2 are measures of how well the data fit parabolic kinetics of

$$\text{Mass change} = k_p t^{1/n} \quad (1)$$

where k_p is the parabolic rate constant, t is time, and n is the reaction order ($n = 1$ for linear kinetics and $n = 2$ for parabolic kinetics). The parabolic R^2 measures how well the data correlate with parabolic behavior using the calculated k_p (with 1 being exact correlation and 0 being no

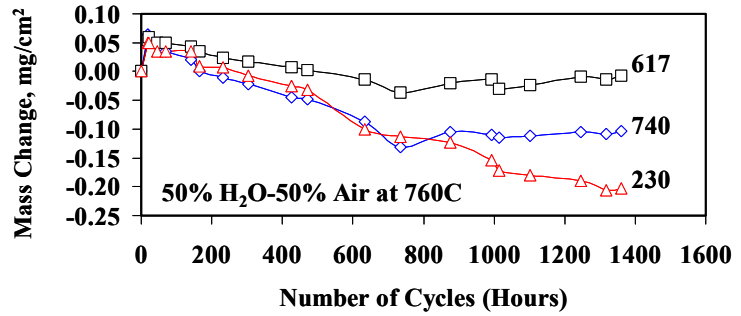


Figure 4. Cyclic oxidation results for nickel-based superalloys at 760°C in 50% H_2O -50% air with hourly cycles.

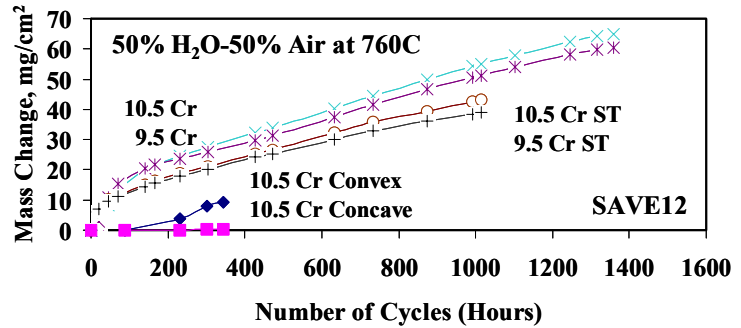


Figure 5. Cyclic oxidation results for The 9.5Cr and 10.5Cr versions of SAVE12 at 760°C in 50% H_2O -50% air with hourly cycles. The curves marked as ST had a proprietary surface treatment on one side of each sample.

Table 3: Thermogravimetric analysis (TGA) for 300 hr tests in O₂-saturated steam plus 60%Ar at 800°C compared with the calculated parabolic rate constant from Sarver and Tanzosh (16) for 4000 hr exposures in O₂-saturated steam at 650°C.

Alloy	%Cr	TGA Results at 800°C			Sarver and Tanzosh (16) 650°C
		Reaction Order, n	Parabolic R ²	Parabolic Rate Constant, k _p mg ² cm ⁻⁴ s ⁻¹	Parabolic Rate Constant, k _p mg ² cm ⁻⁴ s ⁻¹
SAVE12 9.5Cr	9.5	1.78	1.000	1.4×10^{-3}	6.3×10^{-6}
SAVE12 10.5Cr	10.5	1.70	1.000	1.9×10^{-3}	
J1	12.1	1.73	0.990	3.8×10^{-7}	
J5	12.5	1.91	0.990	1.7×10^{-7}	
René 41	19	1.72	0.983	7.2×10^{-7}	
Alloy 617	22	2.63	0.585	3.9×10^{-8}	1.3×10^{-9}
Alloy 230	22	1.78	0.878	6.9×10^{-8}	8.4×10^{-9}
HR6W	23	1.87	0.524	1.1×10^{-8}	6.4×10^{-9}
Alloy 740	24				1.4×10^{-9}

correlation). The parabolic R² values for J1, J5, René 41, and the SAVE12 alloys were quite close to 1, showing excellent correlation with parabolic kinetics and with relatively little noise in the data. The oxidation rates of Alloy 617, Alloy 230, and HR6W were lower, and with more noise in the mass change data, which resulted in lower parabolic R² values.

Also shown on Table 3 is a comparison of k_p values with those of Sarver and Tanzosh (16) for 4000 hr exposures in O₂-saturated steam at 650°C. In this comparison, the nickel-base alloys have k_p values a factor of 5-30 smaller at 650°C than at 800°C. However, the SAVE12 alloy has a k_p value a factor of 220 smaller at 650°C than at 800°C. This large change in kinetics for SAVE12 is probably due to a large reduction in the ability of lower Cr-containing steels to form protective scales at high temperatures such as 800°C.

The results for furnace exposures are shown in Fig. 6 at 700°C and Figs. 7-8 at 800°C. The oxidation rates for the ferritic steel SAVE12 at 800°C (Fig. 7) were quite high, with 10.5Cr having slightly higher rates than 9.5Cr. At 700°C (Fig. 6), the oxidation rates of SAVE12 were much lower; with 10.5Cr showing much less mass increase than 9.5Cr. This is similar to the reported difference between 9% Cr and 12% Cr steels becoming significant at 650°C (17-18).

The nickel alloy J1 at 800°C (Fig. 8) underwent a decrease in mass after about 250 hours. This is currently being examined further to identify the cause. It was not observed in the 300 hour TGA test in steam with 60% Ar. After 600 hr at 700°C (Fig. 6), the mass change with time for J1 has flattened out similar to the higher Cr nickel alloys.

Summary

The status of research to examine the steamside oxidation of advanced alloys for use in supercritical systems was presented. The alloys of interest were mainly nickel-base superalloys, the exceptions being selected high-strength ferritic (SAVE12) and austenitic (Super 304H) stainless steels. The initial results from cyclic oxidation in moist air at 760°C, TGA in steam plus 60% Ar at 800°C, and furnace exposures in moist air at 700°C and 800°C were described:

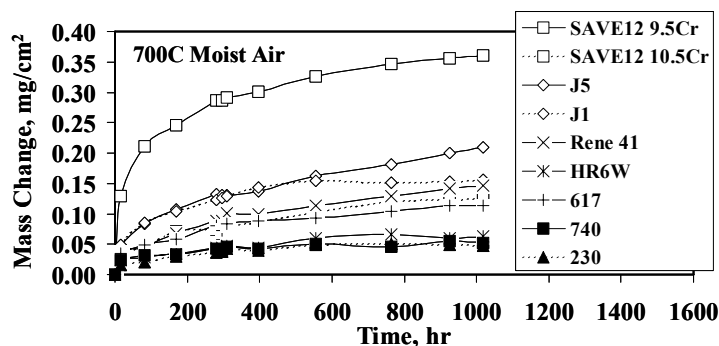


Figure 6. Furnace exposures at 700°C in moist air.

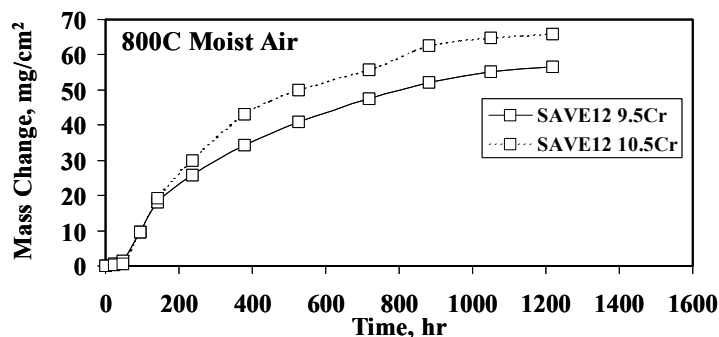


Figure 7. Furnace exposures of SAVE12 at 800°C in moist air.

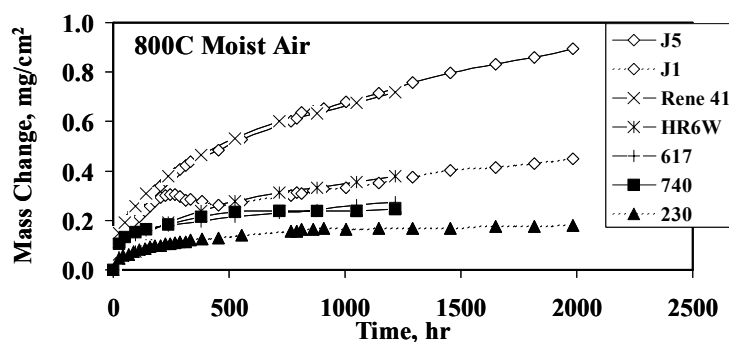


Figure 8. Furnace exposures of nickel-base alloys at 800°C in moist air.

- Cyclic oxidation of nickel-base superalloys indicated a relatively steady rate of oxide scale loss after an initial mass gain. The mass change after 100 hours for Alloy 617, Alloy 230, and Alloy 740 was -0.37 , -1.75 , and -0.88 mg/cm²y, respectively.
- Cyclic oxidation of the ferritic SAVE12 alloys resulted in high oxidation rates with linear kinetics after an initially higher oxidation rate. For the 10.5Cr and 9.5Cr versions of SAVE12 the linear rates were 326 and 296 mg/cm²y, respectively. With a proprietary surface treatment to one side of each sample, the linear oxidation rates were modestly better at 281 and 244 mg/cm²y, respectively.
- Cyclical oxidation of convex and concave SAVE12 with 10.5Cr didn't have an initially large oxidation rate and had linear oxidation rates of 447 and 22 mg/cm²y, respectively.
- TGA tests resulted in measured parabolic rate constants on the order of 10^{-3} mg²cm⁻⁴s⁻¹ for the SAVE12 alloys, 10^{-7} mg²cm⁻⁴s⁻¹ for René 41, J1, and J5, and 10^{-8} mg²cm⁻⁴s⁻¹ for Alloy 617, Alloy 230, and HR6W.
- TGA tests at 800°C in O₂-saturated steam with 60%Ar were compared with much longer furnace exposure tests at 650°C in O₂-saturated steam (16). All of the nickel-base alloys have k_p values a factor of 5-30 smaller at 650°C than at 800°C. However, the SAVE12 alloy had a k_p value a factor of 220 smaller at 650°C than at 800°C. This large change in kinetics for SAVE12 is probably due to a large reduction in the ability of lower Cr-containing steels to form protective scales at high temperatures such as 800°C.
- Furnace exposures gave quite high oxidation rates for the ferritic steel SAVE12 at 800°C, with 10.5Cr having slightly higher rates than 9.5Cr. At 700°C, the oxidation rates of SAVE12 are much lower; with 10.5Cr showing much less mass increase than 9.5Cr.
- Based on these initial oxidation results, the most promising alloys are the high Cr nickel alloys Alloy 617, Alloy 230, Alloy 740, and HR6W. At 700°C, the lower Cr nickel alloy J1 (based on Mitsubishi alloy LTES700) also looks promising.

References

1. B.B. Seth, "US Developments in Advanced Steam Turbine Materials," *Advanced Heat Resistance Steels for Power Generation*, Electric Power Research Institute, 1999, pp. 519-542.
2. *Steam*, 40th ed., Eds. S.C. Stultz and J.B. Kitto, Babcock & Wilcox, 1992, p. 9.
3. R. Viswanathan, A.F. Armor, and G. Booras, "Supercritical Steam Power Plants—An Overview," *Best Practices and Future Technologies*, October 2003, Proceedings (New Delhi, India), National Thermal Power Corporation's Center for Power Efficiency and

Environmental Protection and the US Agency for International Development (USAID), 2003.

4. R. Swanekamp, *Power*, 146 (4), 2002, pp. 32-40.
5. R. Viswanathan, A.F. Armor, and G. Booras, *Power*, 148 (4), 2004, pp. 42-49.
6. G.S. Booras, R. Viswanathan, P. Weitzel, and A. Bennett, "Economic Analysis of Ultra Supercritical PC Plants," *Pittsburgh Coal Conference*, September 2003, Proceedings, (Pittsburgh, PA), University of Pittsburgh, 2003, paper 55.1.
7. G.R. Holcomb, B.S. Covino, Jr., S.J. Bullard, S.D. Cramer, M. Ziomek-Moroz, and D.E. Alman, "Ultra Supercritical Turbines—Steam Oxidation," Proceedings of the 18th Annual Conference on Fossil Energy Materials, U.S. Department of Energy, June, 2004.
8. Y. Tamada, A.M. Beltran, and G.P. Wozney, EPRI Report TR-100979, Electric Power Research Institute, Palo Alto, CA, 1992.
9. R. Viswanathan and W. Bakker, *J. of Materials Eng. and Performance*, 10, 2001, pp. 96-101.
10. D.E. Alman and P.D. Jablonski, Proceedings of the 10th International Symposium on Superalloys, Champion, PA (September 2004) TMS, in press.
11. R. Yamamoto, Y. Kadoya, H. Kawai, R. Magoshi, T. Noda, S. Hamano, S. Ueta, and S. Isobe, "New Wrought Ni-Based Superalloys with Low Thermal Expansion for 700C Steam Turbines," *Materials of Advanced Power Engineering—2002*, Proc. 7th Liege Conf., Sept 30-Oct 3, 2002, Energy and Technology Vol. 21, Forschungszentrum Julich GmbH Inst. Fur Werkstoffe und Verfahren der Energietechnik.
12. R. Viswanathan and W. Bakker, *J. of Materials Eng. and Performance*, 10, 2001, pp. 81-95.
13. M.J. Donachie and S.J. Donachie, *Superalloys: A Technical Guide*, ASM International, Materials Park, OH, 2002, p. 4.
14. J. Sarver, R. Viswanathan, and S. Mohamed, "Boiler Materials for Ultra Supercritical Coal Power Plants—Task 3, Steamside Oxidation of Materials—A Review of Literature," Topical Report, U.S. Department of Energy Grant Number DE-FG26-01NT41174 and Ohio Coal Development Office Grant Agreement D-0020, 2003.
16. J.M. Sarver and J.M. Tanzosh, "Steamside Oxidation Behavior of Candidate USC Materials at 650°C and 800°C," presented at the 8th Ultra-Steel Workshop, Tsukuba, Japan (July 2004).

17. F. Eberle and J.H. Kitterman, Behavior of Superheater Alloys, *High Temperature, High Pressure Steam*, ASME, 1968, p 67.
18. P. Ennis, Y. Wouters, and W.J. Quaddakers, "The Effect of Oxidation on the Service Life of 9-12% Cr Steels," *Advanced Heat Resistant Steels for Power Generation*, Book 798, R. Viswanathan, J.W. Nutting, Eds., IOM Communications, 1999, p 457-467.